

Polymer Communication

A novel rigid-rod alternating poly(*p*-phenylenevinylene) derivative with oligo(ethylene oxide) side chains

Cheng Huang^{a,b,c,*}, Wei Huang^a, Jian Guo^c, Chang-Zheng Yang^c, En-Tang Kang^b

^aInstitute of Materials Research and Engineering (IMRE), National University of Singapore, 3 Research Link, Singapore, Singapore 117602

^bDepartment of Chemical and Environmental Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore, Singapore 119260

^cKey Laboratory of Mesostate Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

Received 11 April 2000; received in revised form 19 October 2000; accepted 24 October 2000

Abstract

A novel yellow-green light-emitting rigid-rod copolymer, poly[(2,5-bis(triethoxy)-1,4-phenylenevinylene)-*alt*-(1,4-phenylenevinylene)] (BTEOPPV-*alt*-PPV) with an alternating structure containing oligo(ethylene oxide) side chains was synthesized by the Wittig reaction of the corresponding triphenylphosphonium chloride and dialdehyde compounds. This soluble and processable copolymer with both electronic and ionic conduction showed good thermal stability as weight loss was less than 5% on heating to about 365°C under nitrogen atmosphere. The DSC thermogram and other relevant measurements showed the liquid crystalline properties and self-ordering in the copolymer. BTEOPPV-*alt*-PPV complexed with metal ions shows an ionochromic effect in the absorption spectrum and also in the electroluminescence spectrum due to the covalent linkage of the oligoethyleneoxy side chains as molecular recognition sites to the PPV backbone, which represents an approach toward chemical sensors. The single-layer light-emitting diode (LED) (ITO/polymer/Al) exhibits an emission maximum at ca 552 nm corresponding to yellow-green emission with a turn-on voltage of 7.5 V and efficiency of 0.038 lm/W (120 cd/m², 10 V, 0.1 A/cm²) while the light-emitting electrochemical cell (LEC) (ITO/polymer + LiOTf/Al) without any extra supporting polymer electrolytes for ionic conduction shows a lower turn-on voltage of 2.5 V, enhanced efficiency of 0.185 lm/W (210 cd/m², 4 V, 0.09 A/cm²) and low response times in the submillisecond range. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ionic conductive alternating poly(*p*-phenylenevinylene); Ionochromism; Light-emitting devices

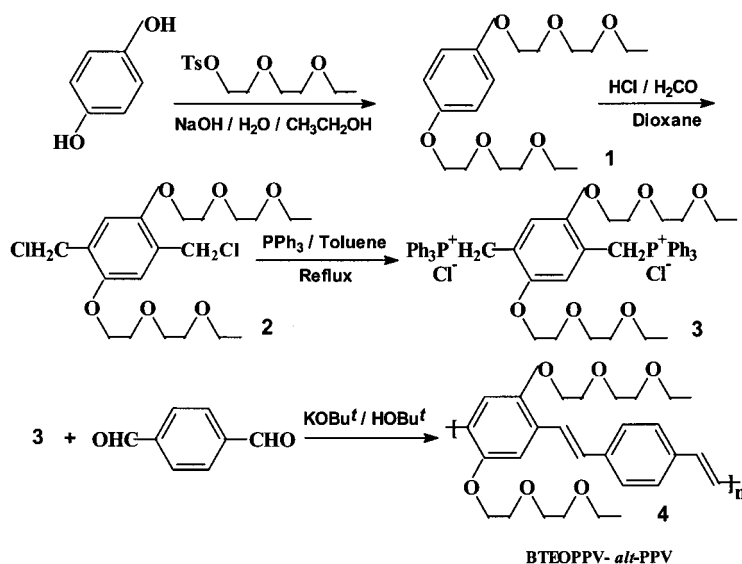
1. Introduction

The discovery of a new generation of light-emitting devices by Pei et al., with mobile ions incorporated into the active polymer layer, has resulted in the introduction of light-emitting electrochemical cells (LECs) [1,2]. These original devices consist of two electrodes and an active polymer layer blended with lithium triflate-doped poly(ethylene oxide) (PEO), which facilitates ionic conductivity. An in situ light-emitting p–n junction was formed by simultaneous p-type and n-type electrochemical doping of electrolyte-containing conjugated polymer chains between two oppositely charged electrodes. Therefore, LECs have many advantages such as low operating voltage, high quantum efficiency, high power efficiency and non-sensibility to the work function of the metal electrodes etc. However, the use

of a polymer blend in these devices can result in phase separation between the emissive layer and the polymer electrolyte, which, in turn, could be detrimental to device performance such as response times, which are necessary for application of LECs in flat panel displays. To overcome this problem, Cao et al. obtained such a bicontinuous network morphology by using a bipolar liquid surfactant in the blend [3]. Pei et al. reported the synthesis of a high-efficiency luminescent polymer, poly[9,9-bis(3,6-dioxaheptyl)-fluorene-2,7-diyl], in which the conjugated poly(1,4-phenylene) main chain is capable of transporting electrons and holes while the grafted bis(3,6-dioxaheptyl) side groups function to solvate ions and promote ion transport as required for high-performance LECs [4,5]. It demonstrated that EL polymers with very polar side chains, such as the oligo(ethylene oxide)-grafted conjugated luminescent polymers [6–27], should be very useful for LEC applications because the polar substituents can act as ionic conducting components to facilitate the electrochemical doping process. The phase separation problem often associated with more conventional LEC devices based on the mixture of polyelectrolyte and π -conjugated polymers could be minimized

* Corresponding author. Institute of Materials Research and Engineering (IMRE), National University of Singapore, 3 Research Link, Singapore, Singapore 117602. Tel./fax: +65-874-8592.

E-mail address: chehc@nus.edu.sg (C. Huang).



Scheme 1.

because of the covalent linkages between the oligo(ethylene oxide) side chains and the conjugated backbone.

While various poly(phenylenevinylene) (PPV) derivatives substituted with alkoxy, alkyl, aryl, halogen, and alkylsilyl side groups have been used in LEDs, some oligo(ethylene oxide)-grafted PPVs have been reported for LEC applications [7–21]. While this work was in progress, we noted that the synthesis and characterization of red or orange-red light-emitting homopolymers or statistical copolymers derived from PPV derivatives with oligo(ethylene oxide) side chains, via the Gilch or sulfonium precursor route for LEC applications, were described in the recent literature [7–18]. In this communication, we present the synthesis for the first time via the Wittig reaction and characterization of a novel yellow-green light-emitting rigid-rod copolymer poly[(2,5-bis(triethoxy)-1,4-phenylenevinylene)-*alt*-(1,4-phenylenevinylene)] (BTEOPPV-*alt*-PPV). This polymer has an alternating structure in which one block is based on *p*-phenylenevinylene and the other unit is linked with 2,5-substituted *p*-phenylenevinylene with ethoxy-terminated oligo(ethylene oxide) side chains. We also present the fabrication and characterization of the light-emitting devices from this soluble and processable copolymer with both electronic and ionic conduction.

2. Experimental

2.1. Synthesis of poly[(2,5-bis(triethoxy)-1,4-phenylenevinylene)-*alt*-(1,4-phenylenevinylene)] (BTEOPPV-*alt*-PPV) (Scheme 1)

2.1.1. 4-Bis(triethoxy)benzene (**1**) and 1,4-bis(chloromethyl)-2,5-bis(triethoxy)benzene (**2**)

Compounds **1** and **2** were synthesized according to proce-

dures given in the literature [28]. The spectroscopic and analytical data were in agreement with the literature values.

2.1.2. 5-Bis(triethoxy)-*p*-xylylenebis(triphenylphosphonium chloride) (**3**)

A solution of 2.20 g (5.0 mmol) of 1,4-bis(chloromethyl)-2,5-bis(triethoxy)benzene and 2.68 g (10.2 mmol) of triphenylphosphine in 40 ml of anhydrous toluene was heated at reflux with stirring for 14 h. The precipitate began separating after 30 min. The mixture was then allowed to cool to room temperature and the gray precipitate was filtered, washed with toluene followed by ether. After drying under vacuum at 60°C, the dry weight was 3.20 g (66%). The powdery white product (m.p. = 246°C) was used for the subsequent polymerization and characterization without further purification. ¹H-NMR (300 MHz, CDCl₃, ppm): δ 7.77–7.48 (m, 30H, Ph C–H), 6.92 (s, 2H, aromatic C–H), 5.00(d, *J* = 13.8 Hz, 4H, ArCH₂), 3.49 (m, *J* = 4.8 Hz, 8H, ArOC₂H₄), 3.35 (m, 8H, OC₂H₄OC₂H₅), 3.23 (q, *J* = 7.0 Hz, 4H, OCH₂CH₃), 1.17 (t, *J* = 7.0 Hz, 6H, CH₃); ¹³C-NMR (300 MHz, CDCl₃, ppm): δ 150.7 (aromatic C–O), 135.3 (Ph *p*-C), 134.7 (Ph O–C), 130.4 (Ph *m*-C), 118.8 (Ph C–P), 117.7 (aromatic C–H), 117.0 (aromatic C–CH₂), 70.7(ArOCH₂CH₂), 70.0 (OCH₂CH₂OC₂H₅), 69.3 (OCH₂CH₂OC₂H₅), 67.8 (OCH₂CH₃), 66.9 (ArOCH₂), 25.7, 25.1 (ArCH₂), 15.5 (CH₃); FT-IR (KBr, cm⁻¹): ν 3403, 3052, 3003, 2967, 2927, 2852, 2767, 1587, 1518, 1483, 1453, 1437, 1316, 1229, 1112, 1061, 1028, 995, 949, 870, 833, 745, 691, 635, 525. Anal. Calcd for C₃₆H₆₂Cl₂O₆P₂: C, 69.78; H, 6.48. Found: C, 69.86; H, 6.52.

2.1.3. Poly[(2,5-bis(triethoxy)-1,4-phenylenevinylene)-*alt*-(1,4-phenylenevinylene)] (BTEOPPV-*alt*-PPV) (**4**)

2,5-Bis(triethoxy)-*p*-xylylenebis(triphenylphosphonium chloride) (2.41 g, 2.5 mmol) and 0.34 g (2.5 mmol) of

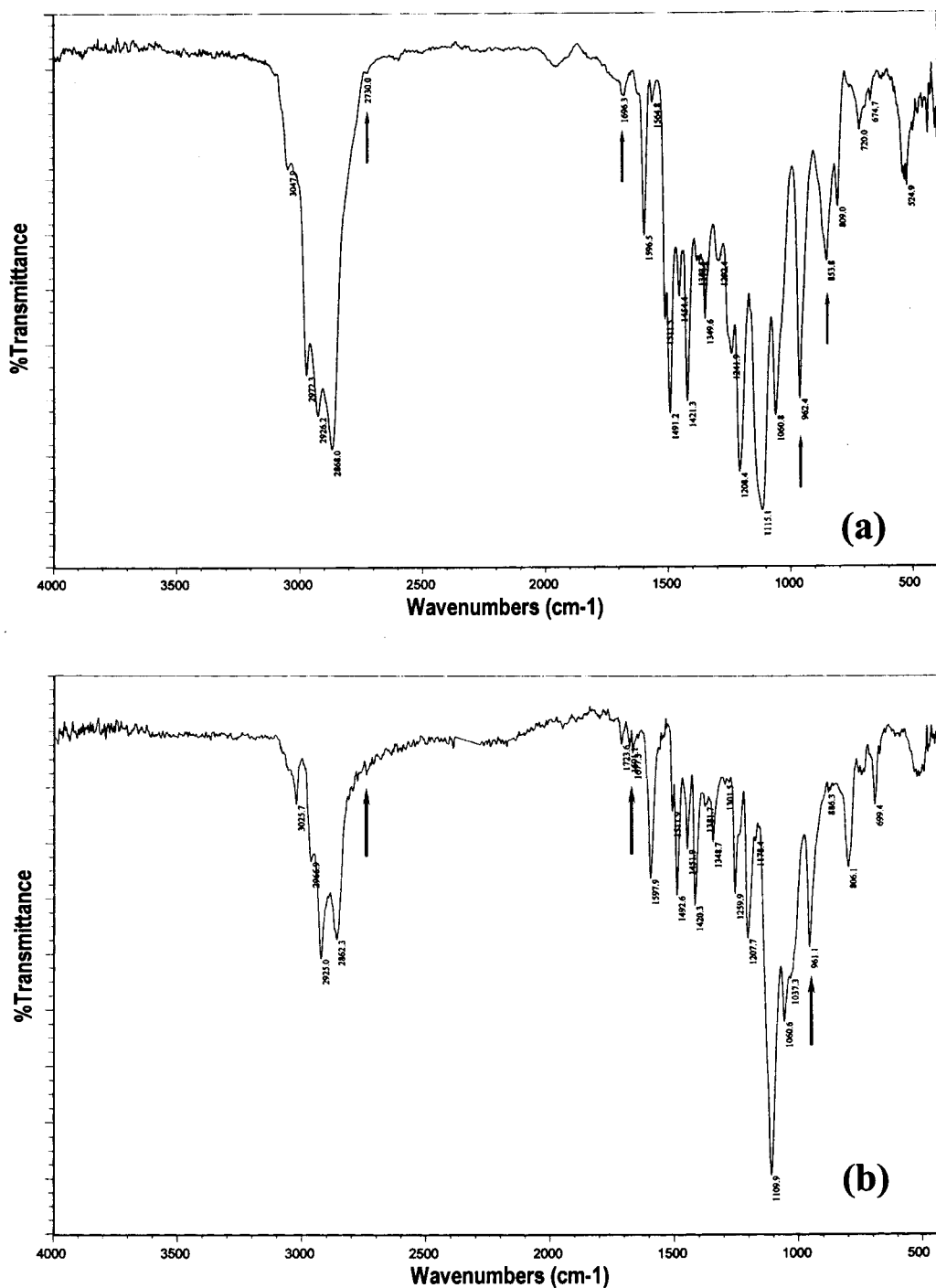


Fig. 1. FT-IR spectra of BTEOPPV-*alt*-PPV film (a) before and (b) after isomerization.

terephthalaldehyde were stirred together in 30 ml of anhydrous *tert*-butyl alcohol at 25°C. A solution of 0.84 g (7.5 mmol) of KOBu^t dissolved in anhydrous *tert*-butyl alcohol (10 ml) was added dropwise under argon over a period of 1 h. An intense orange-red color developed at the point of contact. On mixing, a bright yellow precipitate formed. The mixture was stirred for 10 h. After the addition, the paste-like product was collected and thoroughly washed

with ethanol/water (3/1) to remove the byproducts triphenylphosphine oxide and KCl. After reprecipitation from CHCl₃-MeOH, the orange-yellow solid polymer was dried in a vacuum oven at 40°C to give 0.84 g (72%) of the copolymer. For isomerization of carbon-carbon double bonds into all-*trans* configuration, the orange-yellow solid polymer was refluxed for 4 h in toluene in the presence of a catalytic amount of iodine. After removal of the toluene, the

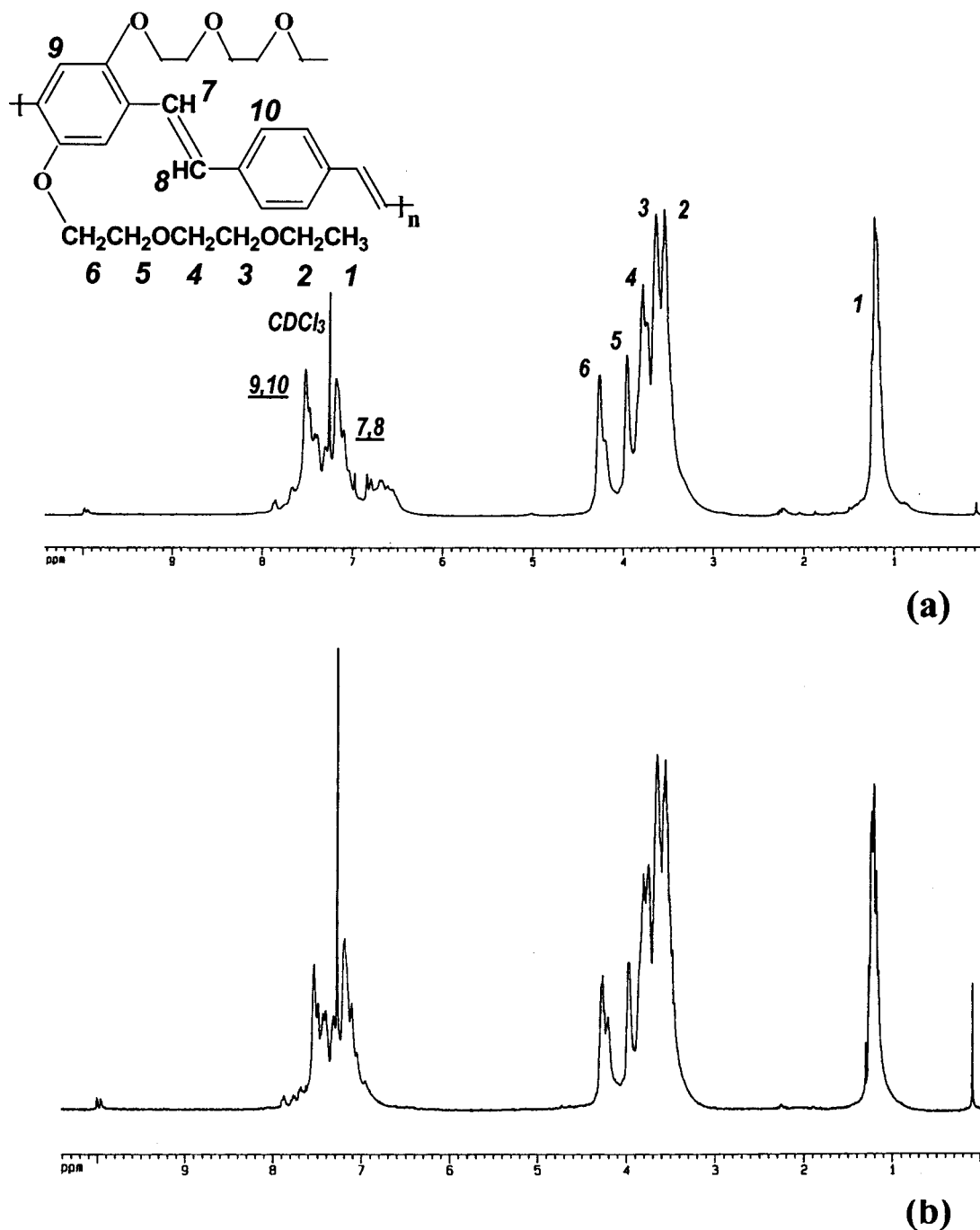


Fig. 2. ¹H-NMR spectra of BTEOPPv-alt-PPV in CDCl₃ (a) before and (b) after isomerization.

product was dissolved in chloroform and precipitated out with methanol. The polymer with all-*trans* configuration was obtained after drying under vacuum [29]. ¹H-NMR (300 MHz, CDCl₃, ppm): δ 7.52 (m, 6H, aromatic protons), 7.10 (m, 4H, vinyl protons), 4.24 (m, 4H, ArOCH₂), 3.97 (m, 4H, ArOCH₂CH₂), 3.78 (m, 4H, OCH₂CH₂OC₂H₅), 3.65 (m, 4H, OCH₂CH₂OC₂H₅), 3.53 (m, 4H, OCH₂CH₃), 1.21 (t, *J* = 6.9 Hz, 6H, CH₃); ¹³C-NMR (300 MHz, CDCl₃, ppm): δ 151.5 (aromatic C–O), 137.5 (Ph C–CH), 129.1 (aromatic

C–CH), 127.3 (Ph C–H), 123.4 (CH=CH), 111.5 (aromatic C–H), 71.4 (ArOCH₂CH₂), 70.3 (OC₂H₄OC₂H₅), 69.1 (OCH₂CH₃), 67.1 (ArOCH₂), 15.5 (CH₃); FT-IR (solution-cast film, cm⁻¹): ν 3025 (aromatic C–H stretching), 2925 (s, ν_{C–H}, CH₃), 2862 (s, ν_{C–H}, CH₂), m, aromatic stretching (1597, 1492), 1451 (m, δ_{C–H}, CH₂), 1420, 1348, 1259, vs C–O–C stretching (1207, 1109, 1060), 961 (*trans*-vinylene C–H, out-of-plane), 806 (m, ν_{C–H}, CH₂), 699. Anal. Calcd for (C₂₈H₃₆O₆)_n: C, 71.77; H, 7.74. Found: C, 71.10; H, 7.78.

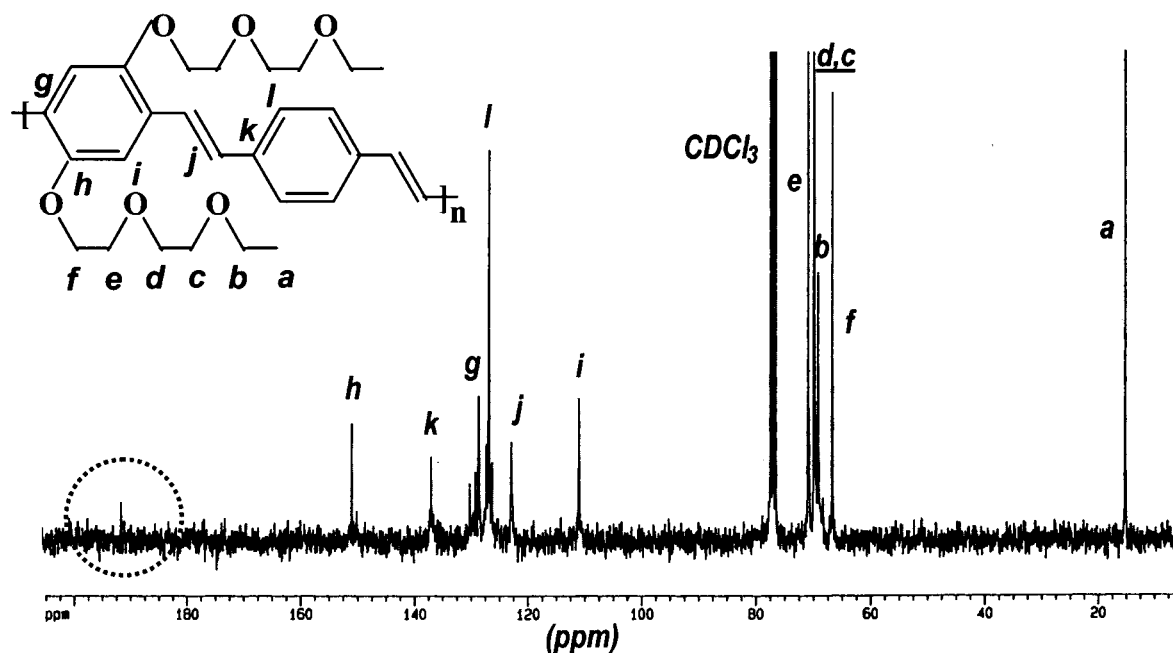


Fig. 3. ^{13}C -NMR spectrum of BTEOPPV-*alt*-PPV in CDCl_3 .

2.2. Fabrication of LEDs

An indium tin oxide coated glass substrate ($50 \Omega/\square$) was washed with water, acetone and isopropyl alcohol sequentially. A yellow-green transparent, pinhole-free thin ($\sim 100 \text{ nm}$) BTEOPPV-*alt*-PPV film, observed by atom force microscopy (Nanoscope IIIa AFM, Digital Instruments), was spin-coated from a 2.0 wt% solution of the polymer in CHCl_3 . Thereafter, an aluminum electrode ($\sim 150 \text{ nm}$) was deposited on top of the device at a high vacuum (below $1 \times 10^{-5} \text{ Torr}$). Wires were attached to the respective electrodes with a conductive carbon colloid. All fabrication steps were performed in clean room conditions. Measurements were done at room temperature. For the LEC fabrication, similar steps were performed except that a film ($\sim 150 \text{ nm}$) was spin-coated from the blend of the copolymer and lithium triflate (LiOTf) (10% w/w to polymer) in chloroform/cyclohexane (5:1 v/v) onto the ITO glass substrate and then heated to 65°C on a hot plate for a few hours to remove any residual solvent.

3. Results and discussion

3.1. Synthesis and characterization of BTEOPPV-*alt*-PPV

BTEOPPV-*alt*-PPV was synthesized through the Wittig reaction of 2,5-bis(triethoxy)-*p*-xylylenebis(triphenylphosphonium chloride) and terephthalaldehyde. The products of each step in Scheme 1 were characterized by spectroscopic methods such as FT-IR (Bruker IFS-66V vacuum-

type FT-IR), ^1H -NMR (Bruker DPX-300 NMR) and ^{13}C -NMR (Bruker DPX-300 NMR). Elemental analyses (Perkin-Elmer EA-240C) were in good agreement with those for the expected structures. The FT-IR spectrum of film BTEOPPV-*alt*-PPV showed the presence of both *cis*- $\text{CH}=\text{CH}$ (853 cm^{-1}) and *trans*- $\text{CH}=\text{CH}$ (962 cm^{-1}) absorptions in medium intensity before isomerization in Fig. 1(a), which indicated that conventional Wittig reaction would create a mixture of *trans* and *cis* isomers while in Fig. 1(b) the pure *trans*-olefins were evidenced by the absence of the characteristic absorbance of *cis*-substituted alkene [29]. It is noteworthy that the IR absorptions of the aldehyde group at 1700 and 2730 cm^{-1} still exist although their intensities are drastically decreased after the polymer has been carefully purified. And aldehyde group was also detected by both ^1H -NMR (9.9 ppm) in Fig. 2 and ^{13}C -NMR (192 ppm) in Fig. 3, which indicated that the polymerization using conventional Wittig reaction was incomplete and the growing polymer chains were terminated by aldehyde groups [30] considering the monomeric residues remaining in the polymers. As depicted in Fig. 2(a), the ^1H -NMR spectrum of BTEOPPV-*alt*-PPV shows the typical resonance of *trans*-substituted vinylene moieties at 7.1 ppm and its *cis*-counterpart in the region at around 6.5 ppm before isomerization while no signal in Fig. 2(b) is observable for *cis*-substituted vinylene moieties after isomerization [31] as shown in the FT-IR spectra. The remaining proton resonances are attributed to the aromatic moiety (7.5 ppm), the ethyleneoxy groups (3.5–4.2 ppm), and the terminal ethoxy group (1.2 ppm). The corresponding ^{13}C -NMR spectrum given in Fig. 3 shows five signals of the aromatic carbons together with the resonances of the olefinic C-atoms at 123.4 ppm

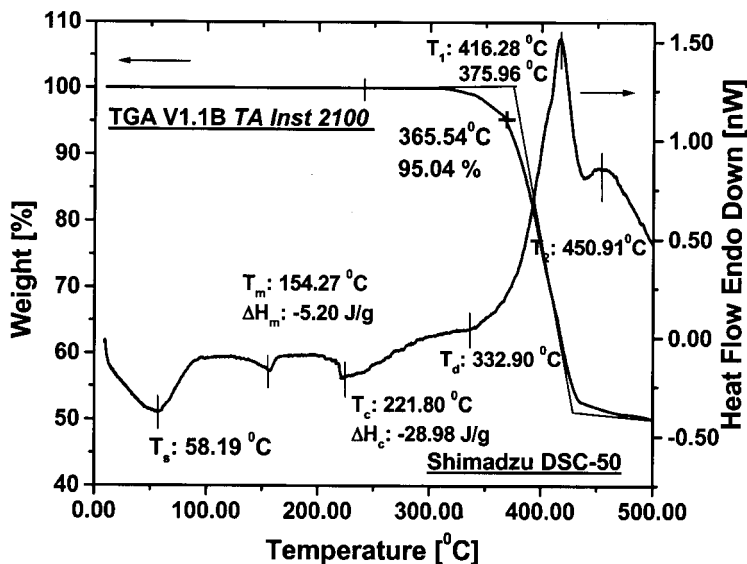


Fig. 4. TGA and DSC thermograms of BTEOPP-*alt*-PPV.

and signals of the aliphatic carbons in the ethyleneoxy units over the range 67.1–71.4 ppm and the ethoxy at 15.5 ppm.

3.2. Physical and thermal properties of BTEOPP-*alt*-PPV

BTEOPP-*alt*-PPV was readily soluble in common organic solvents, such as chloroform, cyclohexane, ethyl acetate, chlorobenzene, toluene and polar and highly polar solvents, such as DMF, pyridine, acetic acid, due to the presence of flexible oligo(ethylene oxide) side chains. These side chains can act as a “bound” solvent lowering the interactions between the main chains and leading to a large increase in entropy when the polymer is dissolved or melted. The molecular weights of the polymer, as determined by gel permeation chromatography (GPC, Waters Model 510) using polystyrene standards, are $M_n = 15,060$

and $M_w = 34,228$ (PDI = 2.27). It was found that BTEOPP-*alt*-PPV had high thermal stability as weight loss was less than 5% on heating to about 365°C under nitrogen atmosphere (Fig. 4) (SDT 2960 Simultaneous DTA–TGA, TA Inst. 2100). The polymer film was stable in air. DSC analysis (Perkin–Elmer DSC-7) revealed that the elastomeric films of BTEOPP-*alt*-PPV have a glass transition temperature (T_g) of 337.4 K from oligo(ethylene oxide) side chains. It was noted that BTEOPP-*alt*-PPV exhibits liquid crystalline properties and self-organization in these materials with rigid-rod *trans*-poly(phenylenevinylene) backbones containing fusible oligo(ethylene oxide) side chains was confirmed by thermal analysis (Shimadzu DSC-50) (Fig. 4), X-ray investigation (Rigaku D/Max-RA XRD) and polarized microscopic observation (ORTHO-LUX-II POL-BK POM equipped with a Leitz hot stage

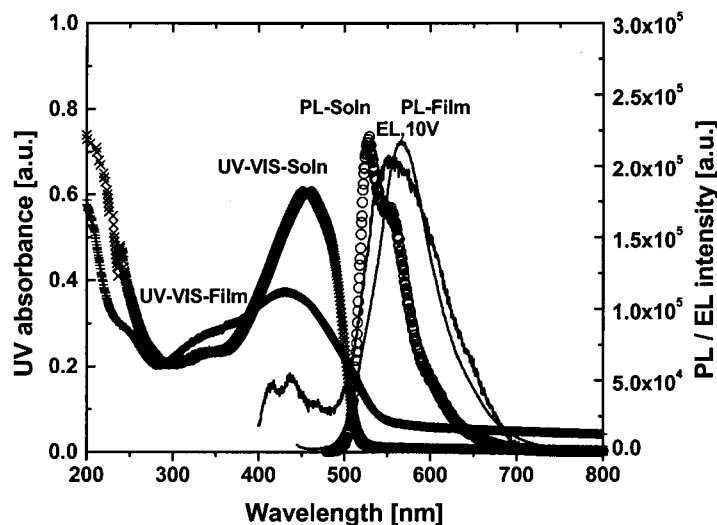


Fig. 5. UV–VIS, PL spectra of BTEOPP-*alt*-PPV film and solution in CHCl_3 , and EL spectrum of the ITO/BTEOPP-*alt*-PPV/Al device.

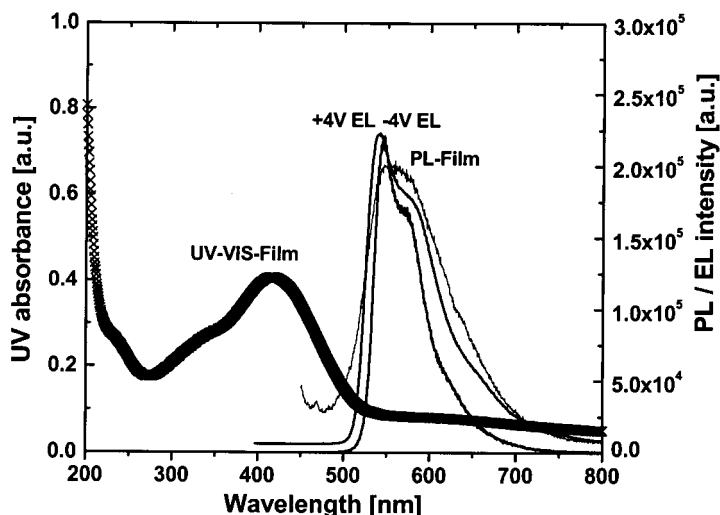


Fig. 6. UV–VIS, PL spectra of LiOTf-complexed BTEOPPV-*alt*-PPV film and EL spectra of the ITO/BTEOPPV-*alt*-PPV + LiOTf/Al device.

and a Wild MPS 51S camera) [32–67]. The work on nanostructure and morphology from self-ordering is in progress.

3.3. Luminescent properties of BTEOPPV-*alt*-PPV

Fig. 5 shows the UV–VIS absorption spectra (Shimadzu UV-3100-VIS–NIR spectrophotometer) of solid film and solution of BTEOPPV-*alt*-PPV. The maximum peaks of the absorption are found at 430 and 455 nm, respectively. The broad, longest wavelength absorbance can be attributed to the π – π^* electronic transition associated with the π -conjugated polymer backbones. The absorption edge is about 530 nm, which corresponds to 2.34 eV of optical band gap close to that of the parent PPV ($E_{\text{opt}} = 2.39$ eV). The broad ground-state absorption spectrum for thin polymer film shows a small blue shift compared to that of the solution spectrum. This small change in absorption spectrum from a thin film to dilute solution is in contrast to many other soluble conjugated polymers where large solvatochromism (the spectra in dilute solution show large blue shifts relative to that obtained in the solid state) has been observed [4,5,28]. Conformational changes of π -conjugated polymers are inherently coupled to the electronic structure of the π -electron system. In the previous literature, polydiacetylenes, poly(thiophene)s and PPVs exhibit color changes (chromism), which is solvent (solvatochromism) and/or temperature (thermochromism) dependent. But the interpretation of these transitions for conjugated polymers has been controversial because of the difficulties in separating the contributions of the conformational changes in the polymer backbone and the aggregation phenomenon of the macromolecules to the observed chromism [68]. However, in BTEOPPV-*alt*-PPV, the side groups that render the polymer soluble are well separated from side groups on the adjacent alternating chromophore unit. The steric interaction between side groups that twists the conjugated repeating units from planar configuration and causes the

solvatochromism is negligible in BTEOPPV-*alt*-PPV. Therefore, this small blue shift in BTEOPPV-*alt*-PPV film compared to the solution spectrum may be the result of solid-state aggregation [30]. It seems that this unusual behavior in the solid state is due to the distortions both in the ether linkage and in the polymer backbone caused by steric hindrances from the enhanced interaction between strong polar neighboring or intermolecular side chains by introduction of additional oxygen atoms [69,70]. Larger contribution of the self-aggregation than electron donation to the π system by oxygen atoms also accounts for the larger band gap of BTEOPPV-*alt*-PPV.

The PL spectra pumped by UV light (JOBIN YVON-SPEX FluoroMax-2 spectrophotometer, $\lambda_{\text{ex}} = 367$ nm, Xe lamp) of thin film spin-coated onto the quartz slide and solution in CHCl_3 display some difference (Fig. 5). The sharp main peak for the solution sample is at 521 nm with a minor shoulder at 550 nm, which is associated with the vibronic coupling of the excitons. While only a main peak for the film sample takes place at 566 nm, which means the emission area lies in the region of yellow-green. The PL quantum efficiency of the polymer measured in a CHCl_3 solution is relatively high ($\Phi_f \cong 0.60$), although the corresponding value for a solid film is only about 10%. The low quantum yield of emission in the thin film can be a result of self-quenching of interchain excimer emission due to stacking (π – π co-facial aggregation) of the polymer [68]. In contrast to the absorption spectra, the emission spectrum was dramatically red-shifted in the thin film relative to solution. The bathochromic shift of the emission maximum in the film is likely due to the highly ordered structure in the solid state film. This ordered structure in the solid state may arise from either intra- or intermolecular π – π interactions of the chromophores. These, in turn, are responsible for the unique optical properties [30]. It is well known that a face-to-face stacking interaction between the phenyl groups can take place in the solid state. However, π – π interactions or

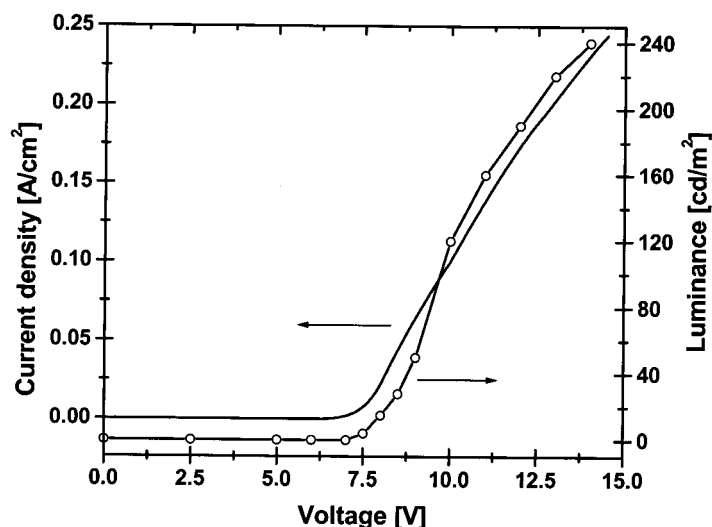


Fig. 7. Current density–luminance–voltage characteristics of a single-layer LED, ITO/BTEOPP–alt–PPV/Al.

stacking depends on the molecular architecture of the polymers (both the chromophore and the nonconjugated flexible chain). The intermolecular stacking may take place in BTEOPP–alt–PPV and strong polar interaction between the intermolecular side chains as well as the planarity of the conjugated backbones controls the stacking morphology [71]. This is consistent with the results obtained from X-ray investigation. Since the polymer forms the stacked structure in the solid state, it is unattractive as a light-emitting device because of its relatively low photoluminescence and electroluminescence quantum efficiencies due to aggregation quenching. Formation of the stacks in the solid state is, on the other hand, an important physical criterion for the formation of liquid crystals. Consequently, the study of BTEOPP–alt–PPV opens up new vistas for theoretical and experimental understanding of such materials and for developing them as liquid crystal devices. This also opens a new way of designing nanosized capacitors and other building blocks for nanoelectronic devices formed by self-assembly processes [72].

It is noted that in the absorption spectrum of BTEOPP–alt–PPV complexed with Li triflate, in the same ratio as it is used in the device, a small shift of the maximum to shorter wavelengths ($\lambda_{\max} = 414$ nm, $E_{\text{opt}} = 2.41$ eV) can be observed (Fig. 6). This shift of the absorption spectrum of LiOTf-complexed BTEOPP–alt–PPV compared with BTEOPP–alt–PPV ($\lambda_{\max} = 430$ nm, $E_{\text{opt}} = 2.34$ eV) (Fig. 5) can be considered to be due to the complexation of the oligoethyleneoxy side chains with Li^+ metal ions. This effect is also known for some other conjugated polymers containing linear or cyclic oligo(ethylene oxide) based molecular recognition sites that can be used as chemical sensors [14,73,74]. These sensor effects are based on the principle that the conformation and/or the electron density of the conjugated polymer backbone change (*ionochromic* or *voltammetric effects*) due to the presence of ions. Upon

ion complexation, conformational defects along the polymer backbone and reduction in the degree of conjugation result in electronic localization leading to a sensory response [13,75]. In addition, the introduction of a salt into the polymer matrix can lead to spatial rearrangement of the polymer chains. So the sensor effects may be partly contributed by the intermolecular restacking in the solid state [37] because the additional salts can be used to control interchain packing distances and the degree of intermolecular excimer formation [71] in terms of supramolecular structure and morphology of the materials. Therefore, such a shift is not only visible in the absorption or PL spectrum but also in the EL spectrum where a similar shift of the electroluminescence spectrum of LiOTf-complexed BTEOPP–alt–PPV in the LEC ($\lambda_{\max} = 541$ nm) (Fig. 6) compared to the electroluminescence spectrum of pure BTEOPP–alt–PPV in the LED ($\lambda_{\max} = 552$ nm) (Fig. 5) as in the absorption is observed. This unexpected behavior, as well as the ion formation, free ions to ion pairs ratio change with temperature and morphology change of this copolymer after adding the extra LiOTf, is currently under investigation.

The single-layer LED based on BTEOPP–alt–PPV shows a yellow-green light EL emission similar to the PL emission of the solid film but with a small hypsochromic shift. This indicates, as expected, the same singlet excitons being responsible for both the EL and PL emissions. Fig. 7 shows the characteristics of the current density and luminance against voltage at the single-layer LED. This LED showed a turn-on voltage of 7.5 V and efficiency of 0.038 lm/W (120 cd/m^2 , 10 V, 0.1 A/cm^2). For the LEC with the structure ITO/BTEOPP–alt–PPV + LiOTf /Al, Fig. 6 shows EL spectra upon application of a voltage of forward-bias or reverse-bias. The spectrum of emitted light is the same in either case indicating that the emission is independent of which electrode serves as the anode and

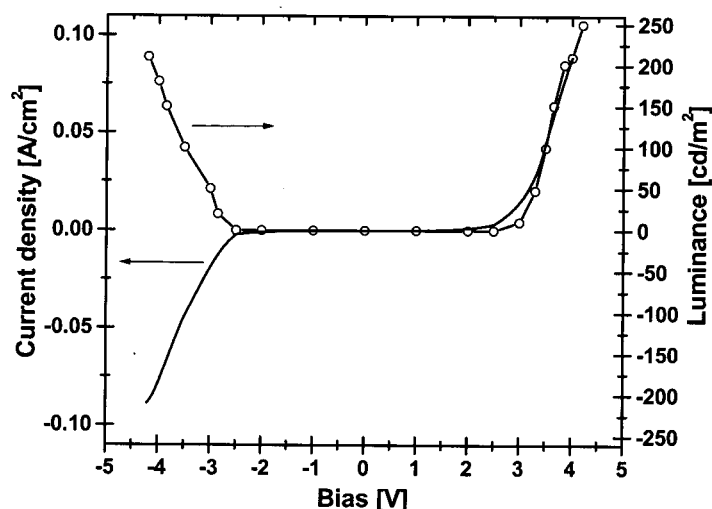


Fig. 8. Current density–luminance–voltage characteristics of a LEC, ITO/BTEOPPV-*alt*-PPV + LiOTf/Al.

which serves as the cathode: the LEC is bipolar. The PL spectrum, included for comparison, is slightly red-shifted, as in the pure BTEOPPV-*alt*-PPV. Fig. 8 shows symmetric current density/V and luminance/V characteristics typical for these kinds of LEC devices. This LEC based on BTEOPPV-*alt*-PPV with alternative building blocks carrying side chains capable of supporting polyelectrolytes shows a lower turn-on voltage of 2.5 V compared with its single-layer LED and enhanced efficiency of 0.185 lm/W (210 cd/m², 4 V, 0.09 A/cm²) much higher than the efficiency of its corresponding LED. Furthermore, the response times of this LEC driven with a square wave form pulse are found to be in the microsecond range, which is low enough for its application in column-row addressable flat panel displays.

Acknowledgements

The authors would like to thank the State Key Laboratory of Solid State Microstructures, Research Center for Nanomaterials Science & Technology, Key Laboratory of Semiconductor Devices & Heterostructures of Nanjing University, and National Flat Panel Display Engineering Center, LCD Department of Nanjing Electronic Devices Institute, for their technical support.

References

- [1] Pei QB, Yu G, Zhang C, Yang Y, Heeger AJ. *Science* 1995;269:1086.
- [2] Pei QB, Yang Y, Yu G, Zhang C, Heeger AJ. *J Am Chem Soc* 1996;118:3922.
- [3] Cao Y, Yu G, Heeger AJ, Yang CY. *Appl Phys Lett* 1996;68:3218.
- [4] Pei QB, Yang Y. *J Am Chem Soc* 1996;118:7416.
- [5] Yang Y, Pei QB. *J Appl Phys* 1997;81:3294.
- [6] Neher D, Gruner J, Cimrova V, Schmidt W, Rulkens R, Lauter U. *Polym Adv Technol* 1998;9:461.
- [7] Hwang D-H, Kim ST, Li XC, Chuah BS, De Mello JC, Friend RH, Moratti SC, Holmes AB. *Polym Prepr* 1997;38:319.
- [8] Chuah BS, Hwang D-H, Kim ST, Moratti SC, Holmes AB, De Mello JC, Friend RH. *Synth Met* 1997;91:279.
- [9] Hwang D-H, Chuah BS, Li XC, Kim ST, Moratti SC, Holmes AB, De Mello JC, Friend RH. *Macromol Symp* 1998;125:111.
- [10] Rost H, Chuah BS, Hwang DH, Moratti SC, Holmes AB, Wilson J, Morgado J, Halls JJM, De Mello JC, Friend RH. *Synth Met* 1999;102:937.
- [11] Morgado J, Cacialli F, Friend RH, Chuah BS, Moratti SC, Holmes AB. *Synth Met* 2000;111-112:449.
- [12] Morgado J, Friend RH, Cacialli F, Chuah BS, Moratti SC, Holmes AB. *J Appl Phys* 1999;86:6392.
- [13] Winkler B, Dai LM, Mau AW-H. *Chem Mater* 1999;11:704.
- [14] Holzer L, Wenzl FP, Tasch S, Leising G, Winkler B, Dai LM, Mau AW-H. *Appl Phys Lett* 1999;75:2014.
- [15] Holzer L, Winkler B, Wenzl FP, Tasch S, Dai LM, Mau AW-H, Leising G. *Synth Met* 1999;100:71.
- [16] Tasch S, Holzer L, Wenzl FP, Gao J, Winkler B, Dai LM, Mau AW-H, Sotgiu R, Sampietro M, Scherf U, Mullen K, Heeger AJ, Leising G. *Synth Met* 1999;102:1046.
- [17] Wenzl FP, Holzer L, Tasch S, Scherf U, Mullen K, Winkler B, Mau AW-H, Dai L, Geising G. *Synth Met* 1999;102:1138.
- [18] Winkler B, Dai L, Mau AW-H. *J Mater Sci Lett* 1999;18:1539.
- [19] He GF, Yang CH, Wang RQ, Li YF. *Displays* 2000;21:69.
- [20] Cao Y, Pei QB, Andersson MR, Yu G, Heeger AJ. *J Electrochem Soc* 1997;144:L317.
- [21] Chen XW, Li ZX, Xie HQ, Li YF. *Chem J Chin Univ* 2000;21:1301.
- [22] Yang Y, Pei QB. *Appl Phys Lett* 1997;70:1926.
- [23] Stephan O, Collomb V, Vial JC, Armand M. *Synth Met* 2000;113:257.
- [24] Lee JI, Hwang D-H, Park H, Do LM, Chu HY, Zyung T, Miller RD. *Synth Met* 2000;111-112:195.
- [25] Johansson T, Mammo W, Andersson MR, Inganäs O. *Chem Mater* 1999;11:3133.
- [26] Kim K, Kim TS. *Polymer-Korea* 1999;23:731.
- [27] Mammo W, Andersson MR. *Bull Chem Soc Ethiopia* 1998;12:141.
- [28] Garay RO, Mayer B, Karasz FE, Lenz RW. *J Polym Sci Part A: Polym Chem* 1995;33:525.
- [29] Pang Y, Li J, Hu B, Karasz FE. *Macromolecules* 1999;32:3946.
- [30] Sarker AM, Strehmel B, Neckers DC. *Macromolecules* 1999;32:7409.
- [31] Memeger Jr. W. *Macromolecules* 1989;22:1577.
- [32] Lauter U, Meyer WH, Wegner G. *Macromolecules* 1997;30:2092.
- [33] Cimrova V, Remmers M, Neher D, Wegner G. *Adv Mater* 1996;8:146.

- [34] Lauter U, Meyer WH, Enkelmann V, Wegner G. *Macromol Chem Phys* 1998;199:2129.
- [35] Baum P, Meyer WH, Wegner G. *Polymer* 2000;965:41.
- [36] Rulkens R, Schulze M, Wegner G. *Macromol Rapid Commun* 1994;15:669.
- [37] Meyer WH. *Adv Mater* 1998;10:439.
- [38] Child AD, Reynolds JR. *Macromolecules* 1994;27:1975.
- [39] Heldmann C, Schuze M, Wegner G. *Macromolecules* 1996;29:4686.
- [40] Heldmann C, Neher D, Winkelhahn HJ, Wegner G. *Macromolecules* 1996;29:4697.
- [41] Vanhee S, Rulkens R, Lehmann U, Rosenauer C, Schulze M, Kohler W, Wegner G. *Macromolecules* 1996;29:5136.
- [42] Yun HC, Chu EY, Han YK, Lee JL, Kwei TK, Okamoto Y. *Macromolecules* 1997;30:2185.
- [43] Gupta VK, Kornfield JA, Ferencz A, Wegner G. *Science* 1994;265:940.
- [44] Esker AR, Mengel C, Wegner G. *Science* 1998;280:892.
- [45] Radler JO, Koltover I, Salditt T, Safinya CR. *Science* 1997;275:810.
- [46] Osterbacka R, An CP, Jiang XM, Vardeny ZV. *Science* 2000;287:839.
- [47] Yu LP, Bao ZN, Cai RB. *Angew Chem Int Ed Engl* 1993;32:1345.
- [48] Bao ZN, Chan WK, Yu LP. *Chem Mater* 1993;2.
- [49] Bao ZN, Chen YM, Cai RB, Yu LP. *Macromolecules* 1993;26:5281.
- [50] Bao ZN, Amundson KR, Lovinger AJ. *Macromolecules* 1998;31:8647.
- [51] Chen XL, Bao ZN, Lovinger AJ, Meer M, Dodabalapur A, Amundson KR, Jakubiak R, Rothberg LJ. *Polym Prepr* 1999;40:1204.
- [52] Bao ZN, Chen XL, Lovinger AJ, Sapjeta BJ. *Polym Prepr* 2000;41:840.
- [53] Pschirer NG, Bunz UHF. *Polym Prepr* 2000;41:460.
- [54] Pschirer NG, Vaughn ME, Dong YB, Loye HCZ, Bunz UHF. *Chem Commun* 2000:85.
- [55] Miteva T, Palmer L, Kloppenburg L, Neher D, Bunz UHF. *Macromolecules* 2000;33:652.
- [56] Pschirer NG, Bunz UHF. *Polym Prepr* 2000;41:405.
- [57] Li AK, Yang SS, Jean WY, Hsu CS. *Chem Mater* 2000;12:2741.
- [58] Winkler B, Tasch S, Zojer E, Ungerank M, Leising G, Stelzer F. *Synth Met* 1996;83:177.
- [59] Hong XYM, Collard DM. *Macromolecules* 2000;33:6916.
- [60] Oguma J, Akagi K, Shirakawa H. *Synth Met* 1999;86:101.
- [61] Lena RW, Furukawa A, Bhowmik P, Garay RO, Majnusz J. *Polymer* 1991;32:1703.
- [62] Crell M, Bradley DDC, Inbasekaran M, Woo EP. *Adv Mater* 1997;9:798.
- [63] Crell M, Bradley DDC. *Adv Mater* 1999;11:895.
- [64] Lussem G, Wendorff JH. *Polym Adv Technol* 1998;9:443.
- [65] Whitehead KS, Grell M, Bradley DDC, Inbasekaran M, Woo EP. *Synth Met* 2000;111–112:181.
- [66] Miteva T, Meisel A, Crell M, Nothofer HG, Lupo D, Yasuda A, Knoll W, Kloppenburg L, Bunz UHF, Scherf U, Neher D. *Synth Met* 2000;111–112:173.
- [67] Clauswitz KUW, Geffarth F, Greiner A, Lussem G, Wendorff JH. *Synth Met* 2000;111–112:169.
- [68] Yan M, Rothberg LJ, Papadimitrakopoulos F, Galvin ME, Miller TM. *Phys Rev Lett* 1994;73:744.
- [69] Chance RR. *Macromolecules* 1980;13:396.
- [70] Chen SA, Tsai CC. *Macromolecules* 1993;26:2234.
- [71] Jenekhe SA, Osaheni JA. *Science* 1994;265:765.
- [72] Thünemann AF. *Adv Mater* 1999;11:127.
- [73] McCullough RD. *Adv Mater* 1998;10:93.
- [74] Leclerc M. *Adv Mater* 1999;11:1491.
- [75] Salaneck WR, Inganas O, Themans B, Nisson JO, Sjogren B, Osterholm JE, Bredas FL, Svensson S. *J Chem Phys* 1988;89:4613.